



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 2719

#### Calcined Petroleum Coke

This Standard Reference Material (SRM) is intended primarily for use in the calibration of apparatus and the evaluation of techniques employed in the analysis of calcined petroleum coke and other materials with a similar matrix. SRM 2719 consists of 50 g of calcined petroleum coke ground to pass a 250  $\mu\text{m}$  (60 mesh) sieve, homogenized, and bottled under an argon atmosphere.

**Certified Values:** The certified values, expressed as mass fractions [1] on a dry basis, are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been investigated or accounted for by NIST. The certified values for aluminum, calcium, iron, nickel, and vanadium are based on two independent NIST methods. The certified value for sulfur is based on a single NIST primary method.

**Reference Values:** The reference values, expressed as a mass fraction on a dry basis are provided in Table 2. The reference values for cobalt and sodium are based on a single NIST method. The values for carbon, hydrogen, and nitrogen are based on a single method performed by the LECO Corporation (St. Joseph, MI) and corroborated by results from the interlaboratory analysis study administrated on behalf of NIST by Laboratory Quality Services International. Reference values are noncertified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty.

**Information Values:** Information values are reported in Table 3. The silicon, ash content, and gross caloric values are based on an interlaboratory analysis study for this SRM, administrated on behalf of NIST by Laboratory Quality Services International. These values are provided without uncertainty for information purposes only.

**Expiration of Certification:** The certification of SRM 2719 is valid, within the measurement uncertainties specified, until **31 December 2010**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is damaged, contaminated, or modified.

The overall direction and coordination of the technical measurements leading to certification were performed by J.D. Fassett and R.L. Watters, Jr., of the NIST Analytical Chemistry Division.

Statistical analysis of the certification data was performed by L.M. Gill and D.D. Leber of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief  
Analytical Chemistry Division

Robert L. Watters, Jr., Chief  
Measurement Services Division

Gaithersburg, MD 20899  
Certificate Issue Date: 01 March 2006  
*See Certificate Revision History on Last Page*

## NOTICE AND WARNINGS TO USERS

**Maintenance of SRM Certification:** NIST will monitor representative samples of this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

## INSTRUCTIONS FOR USE

The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 250 mg should be used for analytical determinations to be related to the certified values and to the reference values for cobalt and sodium. To relate analytical determinations to carbon, hydrogen, and nitrogen reference values, a minimum sample mass of 90 mg should be used. The SRM should be stored in its original, tightly sealed bottle away from sunlight and intense sources of radiation.

**Instructions for Drying:** In order for users to directly relate their measurements to the certified and reference values, drying corrections should be measured and applied at the time of analysis. The correction is determined by drying separate 1 g samples in a nitrogen atmosphere at  $107\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$  to a constant mass. Air is also an acceptable carrier gas for drying this material. The average mass loss measured at NIST for SRM 2719 was 0.07 % (standard deviation = 0.04 %,  $n = 6$ ).

## PREPARATION, HOMOGENEITY, AND ANALYSIS

**Source and Preparation of Material:**<sup>1</sup> The calcined petroleum coke for this SRM was donated by VENCO (Moundsville, WV). The collection of the approximately 240 kg of calcined petroleum coke was under the direction of R.B. Murzyn, Environmental Coordinator, VENCO.

The gross sample was jaw crushed and subsequently pulverized using ceramic plates to pass a 250  $\mu\text{m}$  (60 mesh) screen. The entire lot was then divided using the spinning riffle technique into 48 portions. Sixteen portions were subdivided by the spinning riffle technique into bottles, which were subsequently sealed under an argon atmosphere. The balance of the lot is being retained in long term storage at NIST under an argon atmosphere.

**Homogeneity:** No evidence of inhomogeneity was noted during certification from replicate measurements using the minimum sample size.

Table 1. Certified Values (Dry Basis)

Elements	Mass Fraction (mg/kg)		
Aluminum	58.9	$\pm$	5.7
Calcium	57.7	$\pm$	4.4
Iron	201.6	$\pm$	5.4
Nickel	204	$\pm$	12
Sulfur	8 877	$\pm$	10
Vanadium	58.6	$\pm$	3.4

**Certified Values and Uncertainties:** Certification analyses for aluminum, calcium, iron, nickel, vanadium, and sulfur were performed by the NIST Analytical Chemistry Division. The certified values for aluminum, calcium, iron, nickel, and vanadium are the equally weighted mean of two independent analytical methods. Aluminum, calcium, and vanadium values are based on inductively coupled plasma optical emission spectrometry (ICP-OES) performed by L.J. Wood, and instrumental neutron activation analysis (INAA) performed by D.A. Becker. Iron and

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<sup>1</sup>Certain commercial equipment, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

nickel values are based on ICP-OES performed by L.J. Wood, and INAA performed by R. Demiralp. The certified value for sulfur is based on a single NIST primary method, isotope dilution thermal ionization mass spectrometry (ID-TIMS) [2] performed by W.R. Kelly, J.L. Mann, and R.D. Vocke.

The uncertainty in the concentrations certified by two NIST methods is calculated as  $U = ku_c + B$ , as described by Schiller and Eberhardt [3]. The quantity  $u_c$  is the combined standard uncertainty calculated according to ISO Guide [4], which accounts for the combined effect of the variance for the two methods at one standard deviation. The coverage factor  $k$  is determined from the Student's  $t$ -distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.  $B$  is a bias adjustment for the difference between methods, which is the maximum difference between the certified value and the method means [3].

The uncertainty in the value certified by a NIST primary method is expressed as an expanded uncertainty,  $U$ , and is calculated according to the method described in the ISO and NIST Guides [4]. The expanded uncertainty is calculated as  $U = ku_c$ , where  $u_c$  is intended to represent, at the level of one standard deviation, the combined effect of uncertainty components associated with the measurement and material inhomogeneity, and  $k$  is a coverage factor corresponding to 95 % confidence.

Table 2. Reference Values (Dry Basis)

Elements	Mass Fraction		
Carbon [5]	97.06 %	±	0.92
Cobalt	18.6 mg/kg	±	0.5 mg/kg
Hydrogen [5]	0.16 %	±	0.09
Nitrogen [5]	1.17 %	±	0.05
Sodium	15.1 mg/kg	±	0.9 mg/kg

**Reference Value and Uncertainty:** The reference value for cobalt was determined from INAA performed by R. Demiralp. The reference value for sodium is based on INAA performed by D.A. Becker. The uncertainty in the reference values is expressed as an expanded uncertainty,  $U$ , and is calculated according to the method described in the ISO and NIST Guides [4]. The expanded uncertainty is calculated as  $U = ku_c$ , where  $u_c$  represents, at the level of one standard deviation, the combined effect of uncertainty components associated with the measurement uncertainty and material inhomogeneity, and  $k$  is a coverage factor. The coverage factor  $k$  is determined from the Student's  $t$ -distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte.

The values for carbon, hydrogen, and nitrogen are based on measurements performed according to a NIST experimental plan by the LECO Corporation using ASTM D 5373-93, *Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke* [5]. These results were corroborated by the SRM 2719 interlaboratory analysis study. The uncertainty in the reference values for carbon, hydrogen, and nitrogen are expressed as an expanded uncertainty,  $U = ku_c$ , calculated according to the methods in the ISO and NIST Guides [4] for a prediction interval. The quantity  $u_c$  represents, at the level of one standard deviation, the combined uncertainty due to the potential effects of random measurement errors in the assessment of carbon, hydrogen, and nitrogen and between bottle variance. The quantity  $k = 2$  is the coverage factor used to specify a confidence level of 95 %.

Table 3. Information Values (Dry Basis)

Silicon	138 mg/kg
Ash [6,7]	0.12 %
Volatile Matter [7,8]*	0.54 %
Gross Calorific Value [9,10]	32.90 MJ•kg <sup>-1</sup> (14146 Btu <sub>th</sub> •lb <sup>-1</sup> )

\* Samples having a thermal history above 600 °C, such as SRM 2719, are excluded from the scope of ASTM D 4421-89 [8]. The volatile matter reported may include a loss of mass associated with sample oxidation.

**Information Values:** The information values given in Table 3 for silicon, ash, volatile matter, and gross caloric value are based on an interlaboratory analysis study for SRM 2719, administered on behalf of NIST by Laboratory Quality Services International. Information values are provided without uncertainty for information purposes only.

#### REFERENCES

- [1] Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811, (1995).
- [2] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D.; Chen, L.-T.; *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, p. 2505 (1994).
- [3] Schiller, S.B.; Eberhardt, K.R.; *Combining Data from Independent Analysis Methods*; Spectrochemical Acta, Vol. 46B No. 12, pp. 1607–1613 (1991).
- [4] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed. ISO, Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at <http://physics.nist.gov/Pubs/>.
- [5] ASTM D 5373-93, *Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke*; ASTM Book of Standards, Vol. 05.05, pp. 453–456 (1996).
- [6] ASTM D 3174-93, *Test Method for Ash in the Analysis Sample of Coal and Coke from Coal*; ASTM Book of Standards, Vol. 05.05, pp. 291–294 (1996).
- [7] ASTM D 5142-90, *Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures*; ASTM Book of Standards, Vol. 05.05, pp. 438–442 (1996).
- [8] ASTM D 4421-89, *Test Method for Volatile Matter in Petroleum Coke*; ASTM Book of Standards, Vol. 05.02.
- [9] ASTM D 2015-93, *Test Method for Gross Calorific Value of Coal and Coke by Adiabatic Bomb*; ASTM Book of Standards, Vol. 05.05.
- [10] ASTM D 3286-91a, *Test Method for Gross Calorific Value of Coal and Coke by the Isotherm Bomb Calorimeter*; ASTM Book of Standards, Vol. 05.05, pp. 317–325 (1996).

**Certificate Revision History:** 01 March 2006 (This revision reflects a change from information to reference value for C, H, and N, and an extension of the certification period); 20 May 2002 (Note regarding volatile matter and disclaimer added); 15 July 1999 (Original certificate date).

*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*